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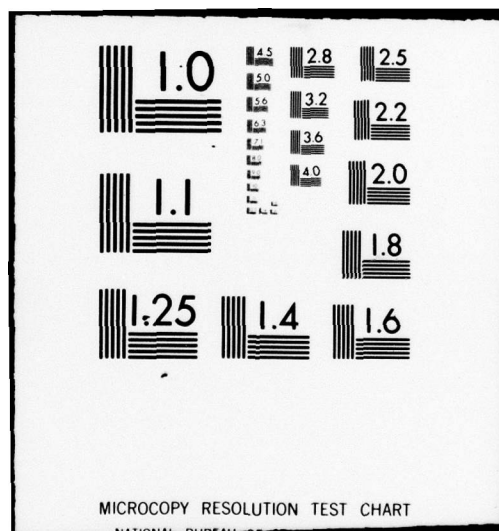
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**Transients in Vibrational Relaxation of Polyatomic Molecules
at High Temperatures by the Variable Encounter Method**

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| <p>→ Temperature dependence of vibrational energy transfer efficiency in high temperature gas systems is described.</p> <p>The Variable Encounter Method is applied to the study of the transient region in vibrational accommodation of cyclobutane at high temperature surfaces. Collision efficiency <u>declines</u> with rise of temperature. Surface collisions are more efficient than binary gas phase encounters.</p> | | |

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Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures
by the Variable Encounter Method

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The study over the past two decades of the collisional de-excitation of highly vibrationally excited reacting neutrals has led to some general findings.¹ They are summarized as follows; obviously, details vary with circumstances from system to system:

1. Relatively strong collider bath gases (M) remove average amounts of energy, $\langle \Delta E \rangle$, of the order of 5-15 kcal mole⁻¹ on each collision.
2. Relatively weak collider bath gases remove lesser amount of energy, say, 0.5-5 kcal mole⁻¹ on each collision.
3. The cross sections for collisional deactivation are closely the same as ordinary gas kinetic cross sections.
4. Energy transfer is primarily V-T,R in nature. Collision complexes are formed, as governed by the attractive forces. Energy in the internal modes of the hot molecule relaxes into the transitional stretching and bending modes that correlate with translations and rotations of the collision partners. Participation of the internal modes of M occurs only if the interaction is strong and the mode spacings of M are intrinsically small.
5. The accommodation between internal modes and transitional modes is restricted by conservation of angular momentum.
6. Monatomic bath gases are less efficient colliders than are diatomic-linear molecules, which are less efficient than polyatomic-nonlinear molecules, in general.

The above generalizations are described by a model given by Lin and Rabinovitch.¹ More recently, a modified, more quantitative version has been given by Battacharjee and Forst.²

Several restrictions should be noted. The first is that the above summary refers to lower temperatures - below 600K-700K where most energy transfer studies of this sort have been made. Very little information is available about the temperature dependence of $\langle \Delta E \rangle$. Two studies have been published at higher temperatures with substrates cyclopropane and cyclopropane-d₂.^{3,4} They reveal that a significant decline in $\langle \Delta E \rangle$ occurs (Table 1).

The second restriction is that measurements have hitherto been restricted to steady state conditions. It is obviously desirable to obtain information in the transient region prior to the establishment of the steady state. Such measurements in a low pressure unimolecular reaction system correspond to the measurement of the mean first passage time.⁵

Finally, there is an intermediate energy region, around 10-30 kcal mole⁻¹, where the energy transfer phenomenon is not well delineated.

We have developed a new technique for the study of neutrals in the transient region. The Variable Encounter Method⁶ (VEM) permits the sequential study of the vibrational relaxation that occurs upon successive collisions of a substrate molecule with a surface. We have reported some preliminary measurements with cyclopropane-d₂.⁷ Besides probing the transient behavior, other information may be gained: the efficiency of the wall has never been explicitly studied; the evidence suggests that it should be more efficient than gas molecules which are of lesser complexity;³ the variation of $\langle \Delta E \rangle$ with temperature can also be probed; finally, whereas previous information has concerned the transition

probabilities in the region around E_0 , the critical threshold energy, VEM is sensitive to the transitions over the whole energy spectrum, including $0 < E < E_0$.

VEM is a very simple technique for studying the dynamics of energy transfer at a surface. Several cylindrical quartz reactor fingers of varying dimensions are blown on to the surface of a large, fused quartz bulb. The fingers may be heated by a stainless block furnace. Entrance area to a reactor finger is $\pm 1/50$ of the bulb area. The dimensions of the reactor used may be varied so as to provide mean wall collision numbers, m , from 2 to 100, per encounter. For a given m , the distribution of wall collisions may be found by Monte Carlo calculation.⁷ Molecules that return to the bulb are cooled by collisions with the bulb wall before another encounter with the reactor occurs.

For the substrates chosen, brief pre-exposure of the heated reactor wall to substrate provided adequate seasoning and reproducible results. To perform a run, one reactor was heated, the bulb (at ~ 375 K) was pumped to a stable residual pressure of $< 10^{-6}$ torr, and substrate was admitted at $1-2 \times 10^{-4}$ torr and left for a suitable time. Analysis was by gas chromatography; percent reaction varied from $\sim 1 - 50\%$.

Experimental energy transfer results are summarized in Table 2. Figure 1a illustrates the variation of \bar{P}_c , the average reaction probability per collision, with m at constant temperature for $c\text{-C}_4\text{H}_8$; the reactor m values were 2.6, 8.5 and 27.2. Figure 1b shows the sequential variation of P_c vs collision number n . The data were fitted by trial with various forms of the collisional probability distribution function, including gaussian and exponential forms having varying detail as a function of E .

We find, in elaboration of our previous results,⁶ that accommodation to a proximate steady state with the wall takes place in a small number of collisions, $\sim 8-30$ for both the cyclopropane and cyclobutane systems (Fig. b), the number increasing with increase of temperature and decrease of $\langle \Delta E \rangle$. Wall collisions on a surface seasoned with a hydrocarbon film are more efficient than are binary gas phase collisions, as may be seen by comparison of Tables 1 and 2. The present data also support our previous findings^{3,4} that energy transfer collision efficiency continues to decline at higher temperatures for these polyatomic unimolecular systems; a turning point at very high temperatures is plausible.

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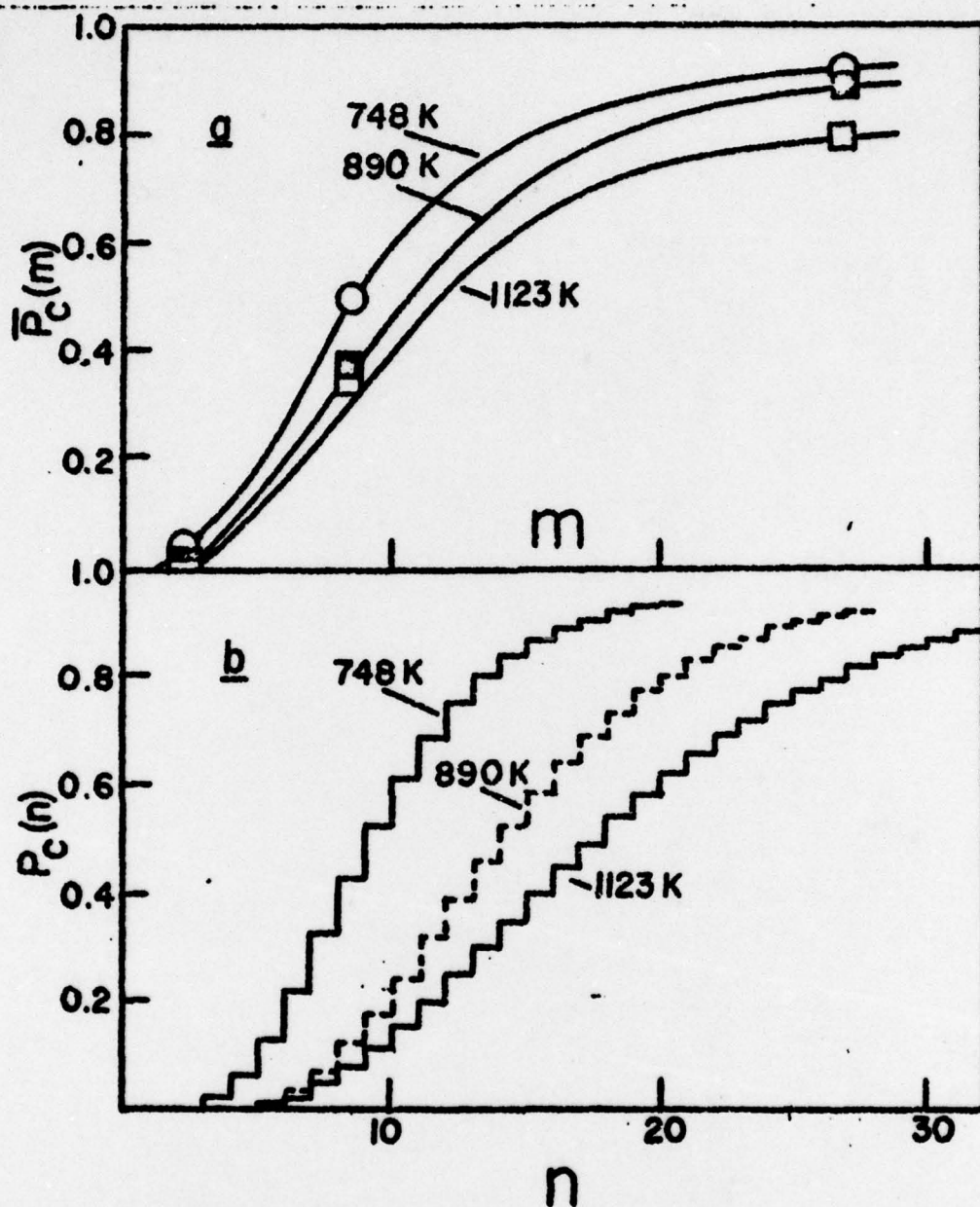


Figure 1a. Plots of experimental average probability of reaction per collision, \bar{P}_c , as a function of mean collision number per encounter, m , at the temperatures indicated. Solid curves are based on trial fit $\langle \Delta E \rangle$ values at various temperatures (Table 2). The ordinate scale is normalized to $\bar{P}_c(\infty) = 1$.

Figure 1b. Plots of $P_c(n)$, the calculated sequential probability of reaction per collision, as a function of the consecutive number of collisions, for the temperatures shown and for the $\langle \Delta E \rangle$ values of Table 2. The ordinate scale is normalized to $P_c(\infty) = 1$.

Table 1. Measurement of $\langle \Delta E \rangle_d$ at Higher Temperatures by Steady State Methods

| Method | Substrate | Bath Gas | T, K | $\langle \Delta E \rangle \text{cm}^{-1}$ | ref |
|--------------------|--|--|------|---|-----|
| CCRS ^a | ξ -1,1- $\text{C}_3\text{H}_4\text{O}_2$ | ξ -1,1- $\text{C}_3\text{H}_6\text{O}_2$ | 775 | $\geq 3000\text{G}^b$ | 3 |
| | | | 975 | 1900G | |
| Diffusion Cloud | ξ - C_3H_6 | CO_2 | 975 | 1100G | 4 |
| | | | 1175 | 450G | |
| | | H_2 | 975 | 400E | |
| | | | 1175 | 350E | |
| | | | 975 | 150E | |
| | | H_2 | 1175 | 90E | |
| | | | 975 | 190E | |
| | | He | 1175 | 160E | |

a) Competitive collisional reaction "spectroscopy";

b) G, gaussian; E, exponential distribution

Table 2. Measurements of $\langle \Delta E \rangle$ at Various Surface Temperatures by VEM

| Substrate | T, K | $\langle \Delta E \rangle \text{cm}^{-1}$ | ref |
|--|------|---|-----------------|
| ξ -1,1- $\text{C}_3\text{H}_4\text{O}_2$ | 800 | 4100G | 7 |
| | 975 | 3400G | |
| | 1175 | 2600G | |
| ξ - C_3H_6 | 800 | 4600G | present work |
| | 960 | 3300G | |
| | 1075 | 2300G | |
| ξ - C_4H_8 | 800 | 2400E | present work |
| | 900 | 1900E | |
| | 1125 | 1500E | |

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